Use of NIR light and upconversion phosphors in light-curable polymers

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Abstract: OBJECTIVE: Light-curable polymers are commonly used in restorative surgery, prosthodontics and surgical procedures. Despite the fact of wide application, there are clinical problems due to limitations of blue light penetration: application is restricted to defects exposed to the light source, layered filling of defect is required. METHODS: Combining photo-activation and up conversion allows efficient polymer hardening by deep penetrating near-infrared (NIR) light. The prerequisite 450 nm blue light to polymerize dental resins could be achieved by filler particles, which absorb the incident NIR irradiation and convert it into visible light. RESULTS: The on spot generated blue light results in uniform polymer hardening. Composite samples of 5mm thickness were cured two times faster than pure polymer cured by blue light (30 and 60 s, respectively). Overall degree of monomer conversion resulted in higher values of more than 40%. The enhanced transmission of NIR light was confirmed by optical analysis of dentin and enamel. The NIR transmittance surge in the 800-1200 nm window could improve sealing of complex and deep caries lesions. SIGNIFICANCE: We demonstrate faster curing and an improved degree of polymerization by using upconversion filler particles as multiple light emission centers. This study represents an alternative approach in curing dental resins by NIR source.

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Use of NIR light and upconversion phosphors in light curable polymers

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Near-infrared curing of dental resins

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Abstract

Objective. Light-curable polymers are commonly used in restorative surgery, prosthodontics and surgical procedures. Despite the fact of wide application, there are clinical problems due to limitations of blue light penetration: application is restricted to defects exposed to the light source, layered filling of defect is required.

Methods. Combining photo-activation and up-conversion allows efficient polymer hardening by deep penetrating NIR light. The prerequisite 450 nm blue light to polymerize dental resins could be achieved by filler particles, which absorb the incident NIR irradiation and convert it into visible light.

Results. The on spot generated blue light results in uniform polymer hardening. Composite samples of 5 mm thickness were cured two times faster than pure polymer cured by blue light (30 and 60 sec, respectively). Overall degree of monomer conversion resulted in higher values of more than 40 %. The enhanced transmission of NIR light was confirmed by optical analysis of dentine and enamel. The NIR transmittance surge in the 800÷1200 nm window could improve sealing of complex and deep caries lesions.

Significance. We demonstrate faster curing and an improved degree of polymerization by using upconversion filler particles as multiple light emission centers. This study represents an alternative approach in curing dental resins by NIR source.

1. Introduction

Light-curing resins have been widely used in restorative dentistry for several decades [1]. These resins are acrylate based and can be polymerized by blue light. They consist of a viscous bisphenol-A glycidyl dimethacrylate (BisGMA), a reactive diluent (triethyleneglycol dimethacrylate, TEGDMA) and a photo-initiator such as camphorquinone [2,3]. The advantage of light-curing over chemical curing in dental applications is that the process is easily controllable and fast. Furthermore, light-curing resins are frequently used in adhesive dentistry to bond ceramic restorations such as inlays, overlays, or crowns to dental hard tissues. However, despite widespread application, these resins suffer from shrinkage [4] and incomplete curing of the resin [5]. The application thickness per treatment is limited by the blue light penetration through dental hard tissue and the polymer itself. Current clinical practice, therefore, relies on layer-by-layer filling of the restorative polymers into a cavity (Fig. 1). The multistep layer-by-layer treatment compels advanced skills in restoration procedures from a dentist and involves long treatment time at considerable costs. Layer-by-layer technique often requires destruction of healthy tooth tissues to provide complete exposure of the restorative towards blue light.

In the present work, we therefore investigate a new way to avoid problems inherent to conventional light-curing dental resins. Deep tissue penetrating near infrared light (NIR) and upconversion (UC) phosphors (a specific class of materials that allows to combine several NIR photons and emit a blue light photon, for review see [6]) can generate the necessary light inside the polymer to homogeneously harden a restorative resin in the tooth. Different energy of the incident NIR irradiation avoids the blue light absorbance loss problem of current dental treatments (Fig. 2a,b).

NIR has recently attracted tremendous interest when dealing with low radiation penetration depth in living tissue [7]. Non-invasive excitation with NIR light has a higher transmittance in the so called “therapeutic window” at 800÷1200 nm [8]. Following such approach, we demonstrate that a clinically relevant dental resin can be cured using NIR light in one step behind various dental hard tissue barriers.

2. Materials & Methods

2.1. Preparation of $NaYF_4$: Yb,Tm particles

The blue emitting hexagonal UC phosphors were prepared by solid state synthesis [9] in the group of Karl Krämer at the University of Bern. Briefly, the rare earth fluorides (YF_3, TmF_3 and YbF_3) were prepared from corresponding oxides by treating them with HF. Sintering the stoichiometric mixtures of derived salts at 550 °C in HF/Ar gas stream resulted in hexagonal $NaYF_4$ host matrix doped with Yb and Tm. The phase composition was analyzed by X-ray diffraction (XRD) recorded on an X'Pert PRO-MPD (PANalytical Netherlands, CuKα radiation, X'Celerator linear detector system, step size 0.033°, under ambient conditions). The derived UC particles were afterwards grounded and analyzed according to protocol (Fig. 3a,b).

2.2. Preparation of Heliobond®/$NaYF_4$: Yb,Tm composites

Polymeric matrix consisted of clinically approved ingredients: adhesive mixture of TEGDMA and BisGMA (40/60%) with camphorquinone as an initiator in Heliobond® (Ivoclar, Vivadent, Liechtenstein) [10]. Powders of UC phosphors were premixed with Heliobond® under different ratios (0/100, 10/90 or 20/80) using a "speed mixer" (Hauschild Eng. DAC 150 FVZ Germany, 3000 rpm - rates per minute) during 30 sec. Then the samples were moulded in cylinders (ø 1 mm) of different thicknesses (1 to 10 mm). Finally, the premixed and moulded specimens were exposed to a NIR laser ($\lambda = 980 \pm 5$ nm, continuous wave, CNI, China) for intervals from 30 seconds to 5 minutes. For comparison, commercial non-filled polymeric samples were cured with blue light ($\lambda = 450$ nm, 550 mW cm^{-2}, Optilux 500, Kerr, USA) for 60 seconds, following the manufacturer's specification.

To evaluate the curing time of pure polymer and composite samples, a needle was manually pressed through the surface of the sample. The absence of a visible needle penetration proved that the sample was hardened.

Scanning electron microscope (SEM; LEO 1530 Gemini, Zeiss, Germany) images characterized the morphology and particles' distribution in the UC phosphor/polymer composites.

2.3. Absolute UC luminescence spectroscopy

Absolute UC luminescence spectra were measured using an integrating sphere (Fig. 3c) following a method described by Ivanova et al. [11]. NIR excitation radiation was delivered through a Ti:sapphire laser pumped by a continuous wave argon ion laser (Coherent Innova 90, USA) and focused on an integrating sphere containing the sample. The excitation power was controlled by a photodiode and adjusted using neutral density filters. The total UC luminescence was collected in a Spectralon™ sphere (Labsphere Inc., USA) with 5 cm diameter (AvaSphere, Avantes BV, Netherlands). The 1 cm diameter sample port was covered with Spectralon™. Emitted light was transmitted by an optical fibre to a spectrometer (AVASpec-1024TEC). The setup (integrating sphere and spectrometer) was calibrated by a halogen tungsten lamp (10 W, fan-cooled Avalight-HAL, Avantes BV, Netherlands).

2.4. Upconversion phosphors preparation and characterization

The UC phosphors were grounded in ball-mill (Pulverisette 7, Tracomme, Switzerland) (10 mm ZrO_2 balls; 1:1 weight ratio) in isopropyl alcohol (technical grade) during 1 to 5 cycles for 30 min. The hydrodynamic particle size distribution was measured (2 wt. %

UC powder in ethylene glycol) using an X-ray disk centrifuge particle size analyzer (Brookhaven Instruments, USA).

2.5. Polymer conversion rate

Cured samples (n = 10) were ground into fine powders by 200 μm corn sandpaper and then mixed with KBr powder (2 wt.%). The absorbance peaks were measured using diffuse reflection in a Fourier transform infrared spectrometer (FTIR, Tensor 27, Bruker Optics, 500÷4000 cm^{-1} wavelength range, resolution 2 cm^{-1}, 64 scans per sample). Non-cured polymer samples were examined with a Bruker Optics Vertex 70v FTIR spectrometer (500÷4000 cm^{-1} wavelength range, resolution 2 cm^{-1}, 64 scans per sample). The degree of conversion of each composite (n = 3) was determined from the ratio of the absorbance intensities of C=C (peak at 1638 cm^{-1}) to one of the C···C (peak at 1608 cm^{-1}) which measures the monomer content before and after curing [12]:

$$DC(\%) = (1 - \frac{\left[\frac{C=C}{C\cdots C}\right]after\ curing}{\left[\frac{C=C}{C\cdots C}\right]before\ curing}) \cdot 100\% \quad (3)$$

2.6. NIR and blue light transmittance of teeth

Bovine enamel and dentin cross-sections of 0.5 mm and 1 mm thickness were analyzed for light transmission. The specimens (n = 5) were stored in water at 5 °C prior to analysis. Samples were examined under dry and wet conditions using an UV-Vis-NIR spectrophotometer (Cary 6000i, Varian, USA).

2.7. Temperature rise

Tooth chamber temperature rise upon curing with NIR laser was measured by K-type thermocouple (Thermocoax, Suresnes, France), which was placed in the prepared cylindrical cavities (1 × 3 mm) at ambient conditions (T = 25 °C). The thermocouple was placed at 1 and 2 mm distance from the cavity filled with resin samples (n = 10) (Fig. 4a).

2.8. Data analysis

All data are stated as mean values ± standard deviation. Statistical significance ($p < 0.05$) between pure polymer and UC phosphors/polymer composite was evaluated by Student's *t*-test for curing performance experiments. Results were taken as significant at $p < 0.05$ for optical parameters for dentin and enamel.

3. Results

Hexagonal sodium yttrium fluoride codoped with ytterbium and thulium [6], i.e. β-$NaYF_4$: 25%Yb^{3+},0.3% Tm^{3+}, was used as UC phosphor. Microcrystalline particles of the pure hexagonal phase (Fig. 3a) were prepared by solid state synthesis [9]. To prevent particles from fast sedimentation in the polymer before curing, ball-milling of the phosphors reduced their mean particle size to 2.8 μm (Fig. 3b). Non-milled powders showed much faster sedimentation in ethylene glycol and BisGMA/TEGDMA polymer leading to inhomogeneous samples.

Since homogeneous hardening of a larger sample requires a good distribution of the light-emitting UC phosphor particles within the polymer matrix, we investigated the even distribution of the UC particles (Fig. 5a). SEM images presented the UC particles of hexagonal morphology (Fig. 5b) in agreement with earlier reports [9] with a size ranging from 2 to 3 μm. This optically determined size range correlates well with the findings from X-ray diffraction (Fig. 3a) and X-ray disk centrifugation (Fig. 3b). The latter method gives an integrated (average, mass-based) hydrodynamic particle size diameter [13], which is the most relevant measure for sedimentation in a suspension.

The UC luminescence spectrum on 980 nm excitation shows mainly the targeted blue emissions with maxima at 457 nm and 480 nm together with a weaker red emission at 652 nm (Fig. 3c). Absolute luminescence spectra revealed maximum spectral irradiance of 50 μW cm^{-2} nm^{-1} measured at 480 nm in the blue spectral range under 160 W cm^{-2} NIR excitation power. Integrating over the peaks of useful radiation between 400-500 nm resulted in a blue light intensity of 1 mW cm^{-2} for 90 W/cm^2 excitation power (Fig. 2c).

The hardening of a 7 mm thick doped polymer slab in a single step was about 3 times faster, than by curing it with a dental lamp (Fig. 6a), even if only the irradiation time is considered. Furthermore, a 0.5 mm enamel plate installed in front of the laser source increased overall curing time for NIR laser and dental lamp cured samples (thickness 2 mm). The UC particles doped composites were set in 45 ± 3 sec, and blue light resulted in almost two times slower curing rate (Fig. 6b). Upon curing the samples with NIR laser, the tooth tissue revealed temperature increase similar to reported conventional blue light curing [14]. The temperature rose by 12 ± 0.35 °C and 10.91 ± 1.6 °C as measured by the thermocouple placed at 1 and 2 mm distances from the cavity, correspondingly (Fig. 4b) .

The maximum degree of monomer conversion (DC) of 42 % was achieved for a NIR cured samples of 2 mm thickness, which is 10 % higher than the DC of the blue light-cured resin (Fig. 6c).The visible absorption spectrum of the light-cured dental resin has a maximum at 470 nm (Fig. 7a), caused by the presence of the polymerization initiator (camphorquinone).

NIR transmission studies revealed increasing transmission for enamel ($\sim\lambda^3$) to longer wavelengths from visible to NIR (Fig. 7b). Calculated attenuation coefficients gave values of $\alpha = 50 \pm 4$ cm^{-1} (n = 5) for dentin and $\alpha = 35 \pm 2$ cm^{-1} (n = 5) for enamel (Table 1).

4. Discussion

Present clinical application of dental acrylates uses a technique where the light-curable resin is applied as multiple layers of 1-2 mm thickness with intermittent blue light irradiation (Fig. 1). This technique at least partially avoids otherwise inhomogeneous curing and shrinkage of the bulk sealants. The viscosity of clinically used acrylates (0.5 to 30 Pa·s [15,16]) generally depends on BisGMA to TEGDMA ratio, filler content and assures negligible particle settling (less than 0.1 mm sedimentation per day [17]) (loss to the bottom of handling vials or during application at the patient) for UC phosphors of a few micron size in spite of their relatively high density (4.5 – 5.3 g cm^{-3} [17]).

Shrinkage is of particular relevance as detachment of the polymer from the tooth surface provides an attractive niche for caries re-infection, a frequently observed clinical incident [18]. Since the here proposed improvement in curing would allow single processing of a tooth lesion, shrinkage is even more critical for good clinical performance. Adjusting the mineral particle content in the composites reduces shrinkage to less than 1 %, which is comparable to commercial filled dental resins (Table 2).

The currently used dental light-curing restorative materials contain mineral additives in the range from 20 to 80 wt.% [19]. The effect of UC phosphor doping was investigated at lower levels of loadings. At 20 wt.% UC phosphor filling, the resulting composite material displayed fast and efficient setting (rapid and homogeneous polymerization throughout the sample). Robustness of the method could be demonstrated by NIR curing over the full range of clinically relevant sample thicknesses from 1 mm (small surface defect in a tooth) to 7 mm.

A fair comparison of the “on spot generated” blue light (from NIR UC) to the currently used dental lamps (also emitting blue light) requires quantification. A so-

called Spectralon^{TM} sphere was used to quantify the luminescence irradiation power of pure, compacted $NaYF_4$: Yb, Tm pills. UC emission intensity increases non linearly with NIR excitation power, as observed in more fundamental, previous studies using similar phosphors [9]. For comparison, the widely used clinical Optilux 500 blue lamp for light-curing dental materials provides a much higher irradiance of 200-300 mW cm^{-2} [20]. Despite its much weaker intensity of 1 mW cm^{-2}, the blue light emitted from the UC particles successfully cures the acrylate polymer.

NIR-assisted curing could significantly reduce treatment time in dental practices. In a clinical setting, one has to add the time to re-apply additional layers. The curing time of 1 mm and 2 mm thick samples was not significantly different for the dental lamp and NIR laser cured samples (Fig. 3a). That is expected from the typical penetration depth of blue light (2-3 mm) allowing the light to reach the whole sample.

The exothermic effect of the light-curing resin polymerization and significant energy absorption during irradiation lead to temperature increase of the restorative and heat up the surrounding tissue, which is unfavourable from a clinical prospective. Curing by NIR laser the composite resin although did not rise the chamber temperature significantly higher than the reported values for curing by a conventional dental lamp [14]. The elevated temperatures upon curing still remain within physiologically acceptable temperatures (Fig. 4b).

The curing time and sample thickness impacts the degree of monomer conversion (DC) in polymerization and was investigated for samples with a fixed loading of UC phosphors. Since monomer curing happens in the bulk of the material, the homogenous light emission from the UC phosphor particles, distributed throughout the sample, provides higher curing rates. For better illustration, one may consider the

mean distance the blue light has to travel before polymerization is initiated (i.e. activating the photo-labile initiator): the blue light emitted by the UC phosphor particles only needs to cross the acrylate sample over several microns, i.e. the average particle distance. For curing the resins with blue irradiation, the light travels the path from the surface to the interior of the material (i.e. about the sample thickness of several millimetres). The visible spectrum of the light-cured dental resin has an absorption maximum at 470 nm (Fig. 6a), caused by the presence of the polymerization initiator (camphorquinone). The reported depth of blue light penetration normally does not exceed 2-3 mm [21] which limits the depth of cure. However, for the NIR region, experiments did not show any strong absorption peaks, therefore, allowing efficient penetration of the light through the sample. Each upconversion particle serves as an emitting centre. For efficient curing of the polymer, generated blue light travels the path equal to the distance between the phosphors, therefore the absorption effect is significantly weaker compared to the conventional curing of the resin by the dental lamp. Note that any classical strategy to solve this problem of sample transparency is bound to fail since any photo-activator must absorb light to actually trigger the polymerization. That means, making a non-absorbing photo-activator is per se impossible, as no absorption would induce no reaction. The presently used clinical material is a delicate balance between high power irradiation (to drive at least some light down to the lower parts of the 1-2 mm sample) and keeping the photo-initiator loading low (i.e. higher transparency) whilst maintaining a clinically reliable and robust degree of polymerization (i.e. mechanical stability, acceptable leaching of non-cured monomers, shrinkage).

Treating complex shaped caries lesions with light cured dental resin often requires cavity opening for light beam penetration. This voluntary destruction of otherwise still healthy tissue stays in contrast to the clinical philosophy of minimizing treatment damage [22]. Ideally, complex caries lesions would only be cleaned and directly filled with polymer, then irradiated through the tooth wall itself. We therefore performed preliminary curing tests on the composite material behind enamel and dentin obstacles as an accurate way to demonstrate a broad range of clinical situations. The curing time of such composites is significantly shorter, because of the improved NIR light penetration through the dental tissues. A 0.5 mm enamel obstacle placed between the light source and the sample decreased the light intensity and therefore resulted in longer curing times. The curing time is significantly shorter for the UC phosphor composites than for samples cured by a blue light source (Fig. 3b).

NIR irradiation has a better penetration through the hard tissues compared to visible light, which results in a so called therapeutic window around 800-1400 nm [23]. The absorption coefficient of dentin in the visible light range is μ_a = 4 cm^{-1}[24]. Following previous studies on the optical properties of hard tissues, the penetration depth could be calculated as:

$$\delta = \frac{1}{\sqrt{3 \cdot \mu_a \cdot (\mu_a + \mu_s')}} \quad (1)$$

where δ denotes the penetration depth of light, and μ_a and μ'_s denote the absorption and reduced scattering coefficients, respectively. The reduced scattering coefficient depends on the anisotropy and is defined as:

$$\mu_s' = (1 - g) \cdot \mu_s \quad (2)$$

where μ_s denotes the scattering coefficient and g is an anisotropy factor.

The penetration depth depends on the reduced scattering and absorption coefficients; therefore, it also correlates with the attenuation coefficient. Consequently, for enamel, the maximum light penetration depth was 6.8 ± 0.5 mm (Table 1), whereas dentin showed a shorter penetration depth of 3.8 ± 1.8 mm. Those values exceed more than twice the numbers reported for the visible range: 2.6 mm for dentin [25] and only 0.7 mm for enamel [26,27].

5. Conclusion

As a result of these studies, we suggest a novel technique for the polymerization of light-curing resins: blending the resins with UC phosphor particles and curing the material with blue UC emission upon NIR excitation. This appears to be a promising approach for single stage dental restorative treatment in spots that are not accessible to direct light. The composites containing UC particles showed shorter curing times and higher degrees of monomer conversion in comparison to the polymer curing by blue light. The depth of NIR light transmission through teeth tissues is higher than that of blue light (450 nm). For this reason, the prepared composites could restore cavities up to 7-10 mm depth in one step, even positioned behind thin enamel or dentin obstacles. Accordingly, these materials may substitute commonly used light-curing polymers, providing additional advantages.

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Figure captions

Fig. 1 - Treatment of caries lesions (dark area, I) using blue light induced curing (II) demands a time consuming layer by layer application and hardening with possible shrinkage and reinfection. Generating blue light inside the polymer through irradiation by near infrared (NIR) allows polymerization in one single step. Since tooth tissue is quite transparent to NIR, irradiation of larger and complex defects proceeds more reliable and can be initiated through irradiation through the tooth sides.

Fig. 2 - (a) Light activated polymerization in a bulk sample requires light to reach all parts of the material (top) which limits sample size as most polymers and photo-initiators strongly absorb the required short-wavelength blue light. Generation of the blue light on spot, throughout the sample (bottom) can be realized through upconversion of several NIR photons to yield one blue light photon. This approach combines deep sample NIR penetration with reliable generation of blue light throughout the material (b, bottom). The blue light emission intensity strongly depends on the NIR excitation power (c)

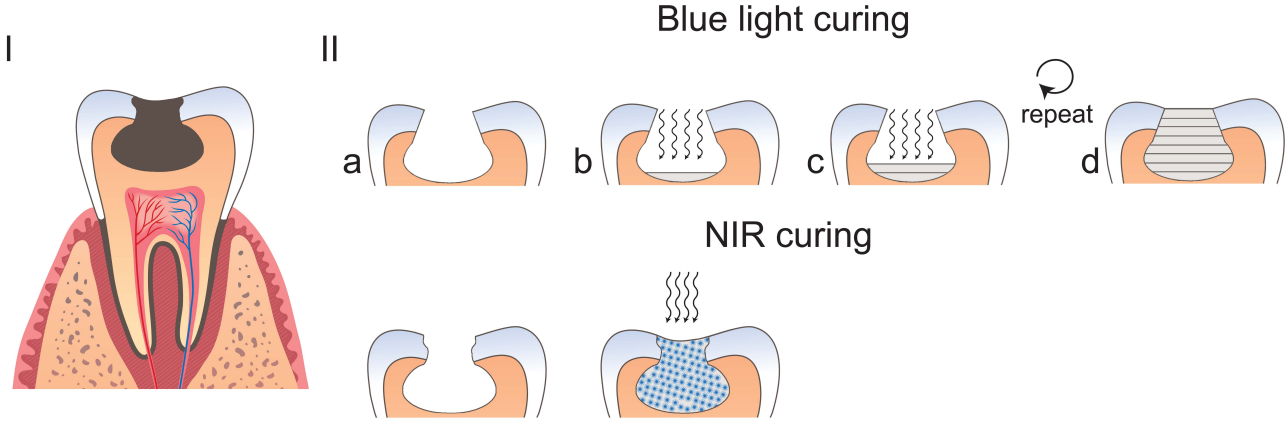
Fig. 3 - $NaYF_4$:Yb,Tm particles characterization. (a) XRD spectrum; (b) Particle size distribution; (c) Spectral irradiance of upconversion phosphors under different excitation powers.

Fig. 4 - (a) Two thermocouples were placed at 1 and 2 mm distances from the tooth cavity filled by composite resin and cured by NIR laser. (b) Temperature increase upon curing by NIR laser and blue light (*) [14].

Fig. 5 - SEM micrographs of polymer/UC phosphor composite: (a) cross-section and (b) magnified view of UC particles incorporated in polymer.

Fig. 6 - (a) Polymer curing times to harden samples of 1 to 10 mm thickness when using blue light (squares) and NIR irradiation (spheres). (b) Dental polymer curing through a side wall of a tooth, modeled by putting an enamel platelet between sample and radiation source. (c) The quality of a polymerization can be quantified through the degree of monomer conversion (DC) and can be significantly improved when generating blue light throughout the sample using upconversion and NIR irradiation.

Fig. 7 - (a) Visible absorption spectrum of BisGMA/TEGDMA resin prior to polymerization. (b) NIR light transmission for enamel and dentin samples (n = 5).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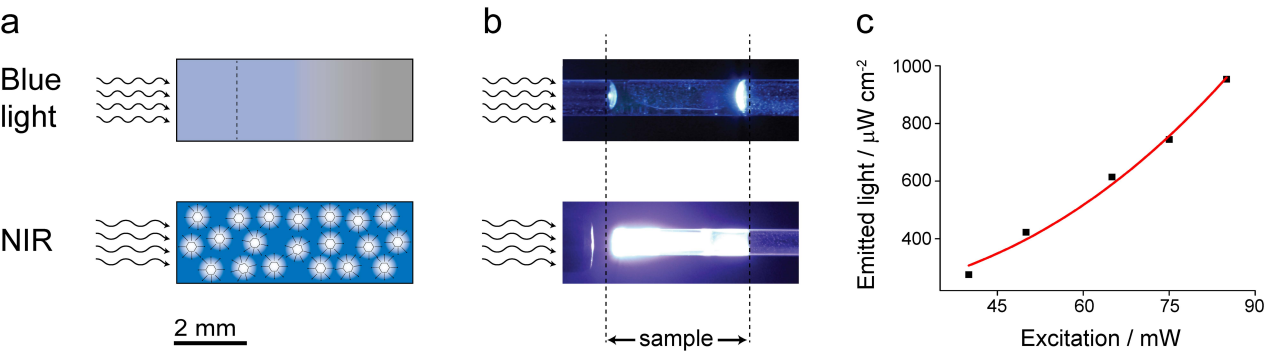
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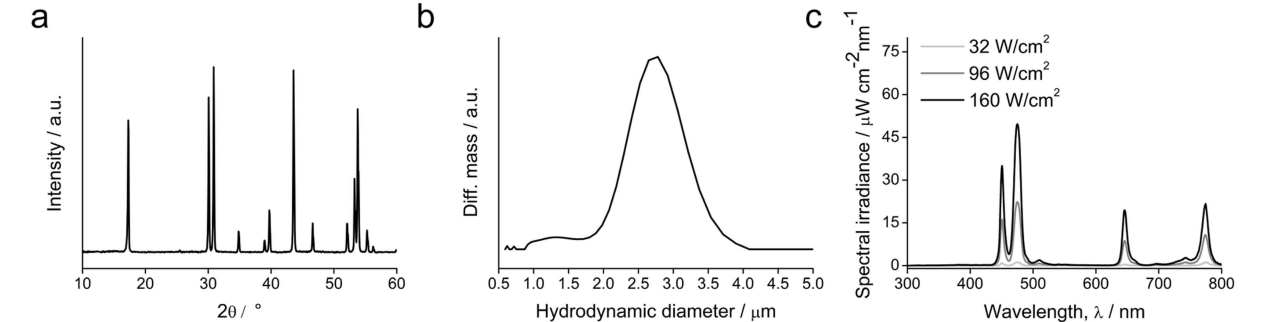
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96 W/cm2
160 W/cm2
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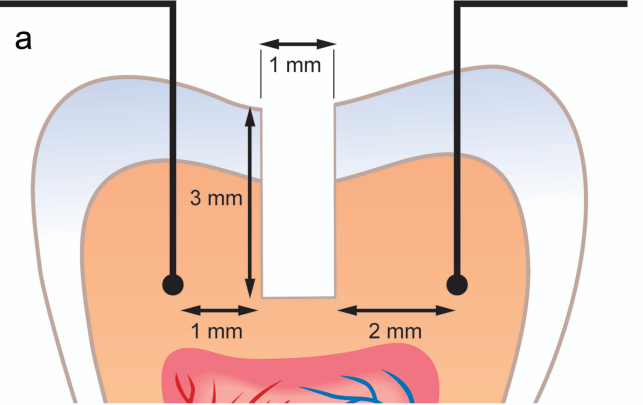
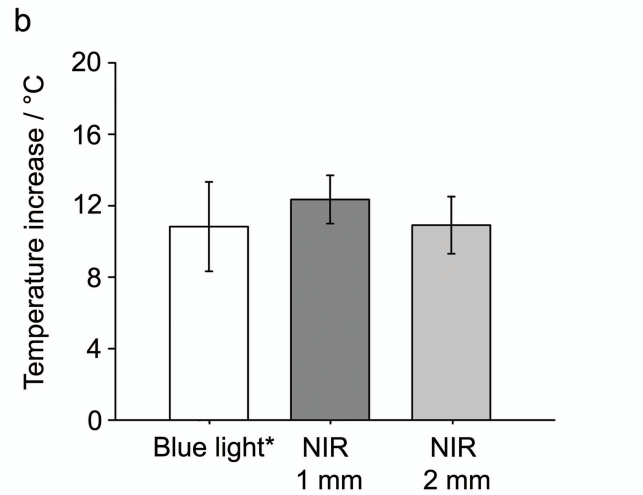
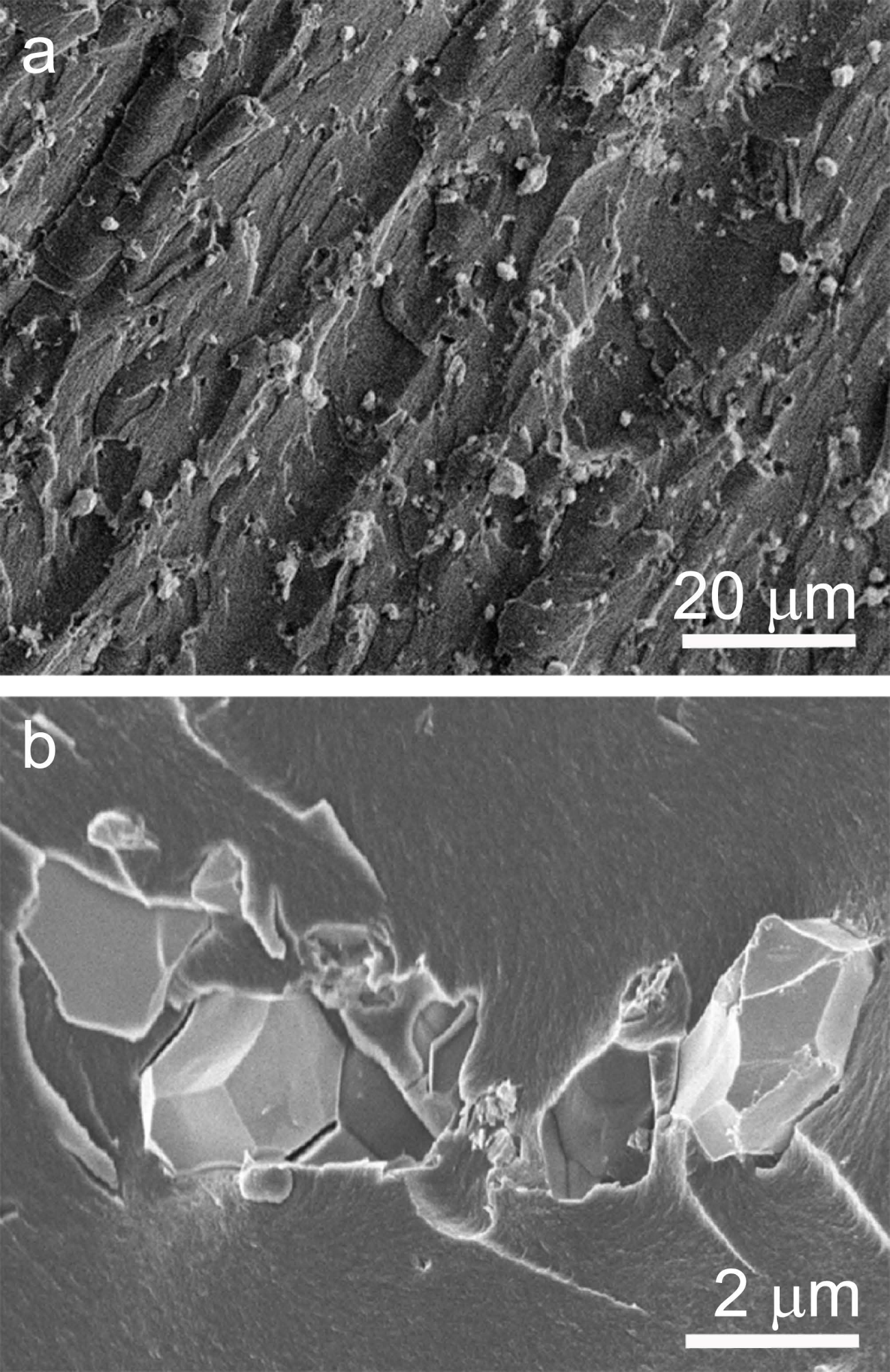
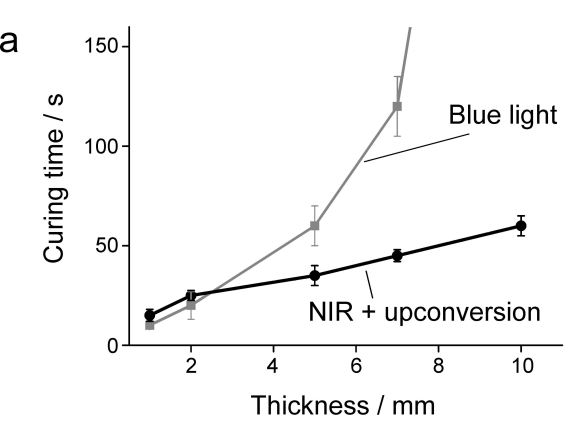
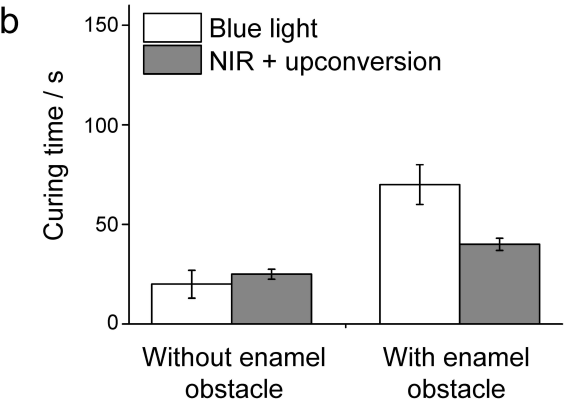
800
Wavelength, λ / nm

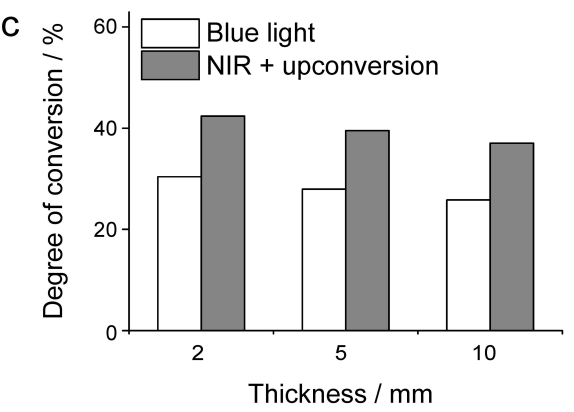

a
1 mm
3 mm
1 mm
2 mm

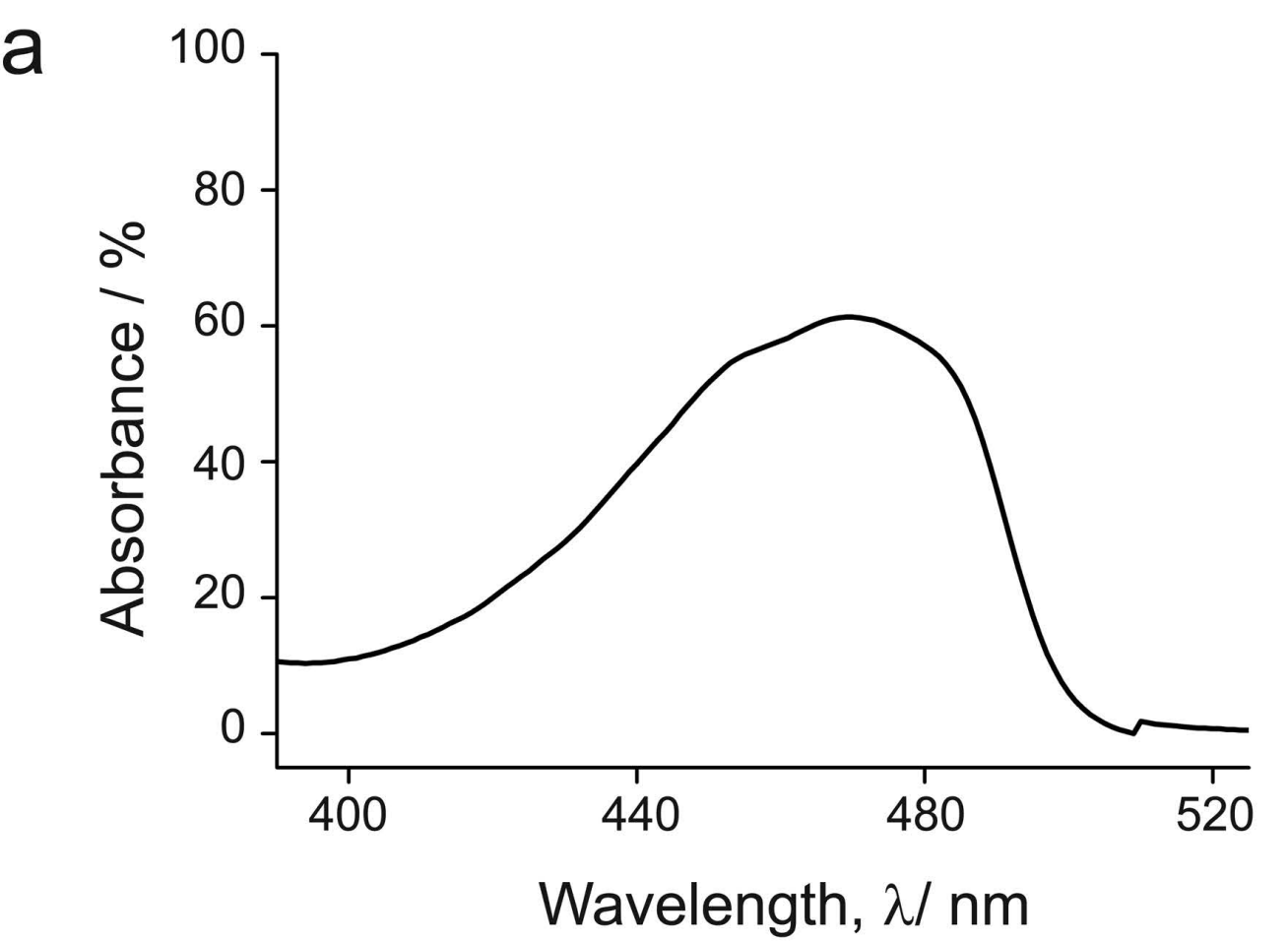

b
Temperature increase / °C
20
16
12
8
4
0
Blue light*
NIR
1 mm
NIR
2 mm


a
20 μm
b
2 μm


a
Curing time / s
150
100
50
0
2
4
6
8
10
Thickness / mm
Blue light
NIR + upconversion


b
Curing time / s
150
100
50
0
Blue light
NIR + upconversion
Without enamel obstacle
With enamel obstacle


c
Degree of conversion / %
60
40
20
0
Blue light
NIR + upconversion
2
5
10
Thickness / mm


a
100
80
60
40
20
0
Absorbance / %
400
440
480
520
Wavelength, λ/ nm

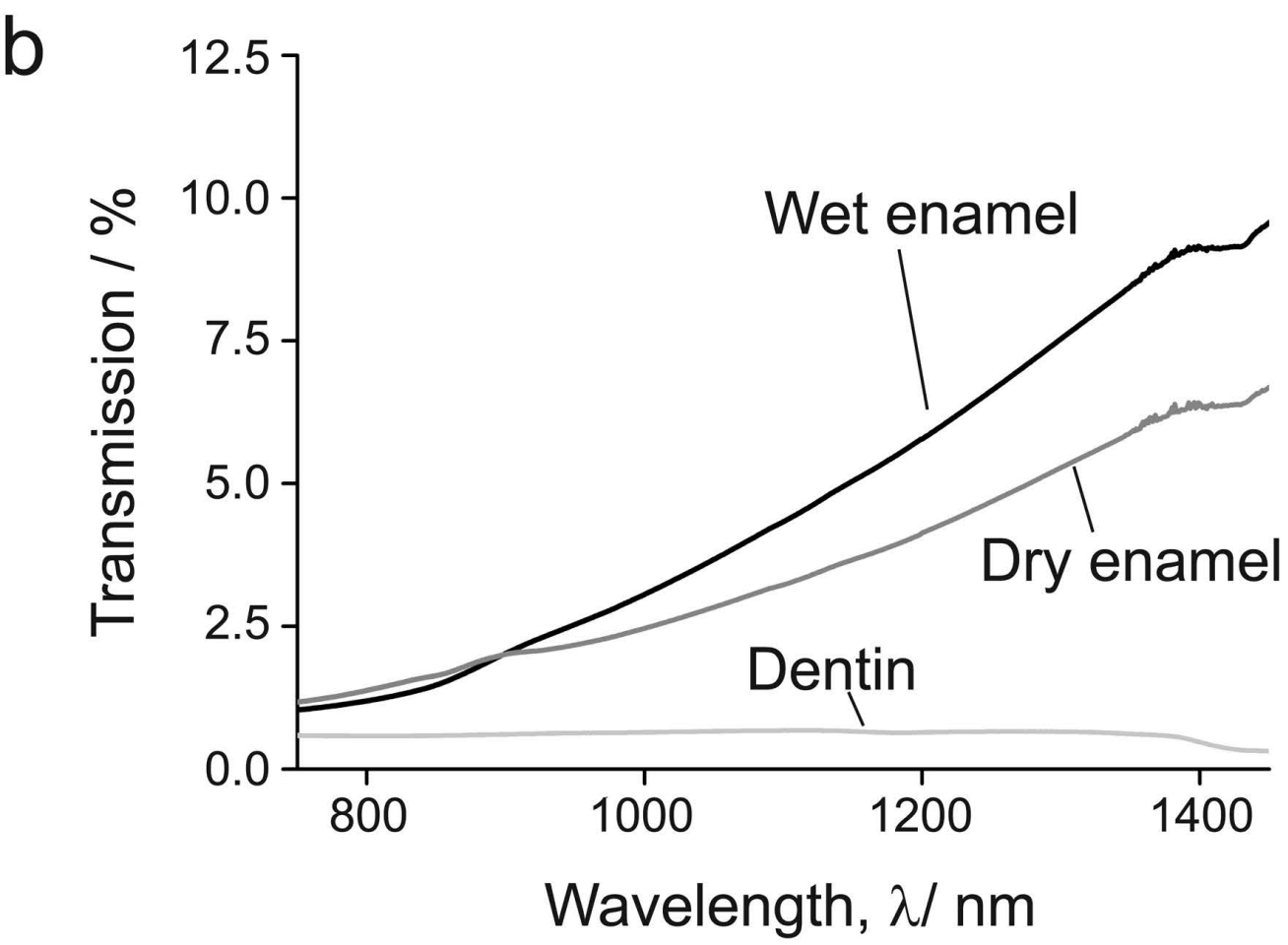

b
12.5
10.0
7.5
5.0
2.5
0.0
Transmission / %
Wet enamel
Dry enamel
Dentin
800
1000
1200
1400
Wavelength, λ/ nm

Table 1. Optical properties of enamel and dentin.

	Attenuation coef.* / cm^{-1}	Anisotropy factor ** / -	Optical penetration depth / mm	
			λ= 980 nm#	λ= 450 nm#
Enamel	35 (2)	0.96	6.8 (0.5)	2.6
Dentin	50 (4)	0.93	3.8 (1.8)	0.7

*Calculated from NIR transmission spectra, **From [26], #Calculated according to [24,25,27]

Table 2: Polymerization shrinkage (n = 5).

	Polymerization shrinkage
Blue light cured resin	5.5 (0.5)
NIR cured resin with 20 wt. % UC particle filler	0.5 (0.3)
BisGMA/TEGDMA = 70/30 polymer	7.04 (0.8)*
BisGMA/TEGDMA = 70/30 polymer with 75 wt. % particle filler	1.94 (0.23)*

* Shrinkage data according to [15]